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(54) A PROCESS FOR THE PREPARATION OF AMIDE-ACID DERIVATIVES OF α,β -UNSATURATED DICARBOXYLIC AND ANHYDRIDE COPOLYMERS

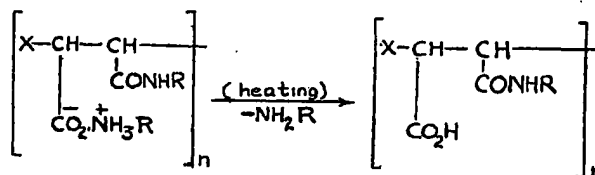
(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of amide-acid derivatives of alternating vinyl or vinylidene/dicarboxylic anhydride copolymers which form water-soluble or water-swellaable salts.

The amide-acid derivatives prepared by the process of the invention are particularly useful as thickening agents. Especially valuable thickening agents are the amide-acid derivatives of methyl vinyl ether/maleic anhydride copolymer.

In accordance with the process of the invention these amide-acid derivatives are prepared by heating substantially anhydrous water-soluble or water-swellaable amide-ammonium or alkyl-substituted amide-alkylammonium salt of an alternating copolymer of an α,β -unsaturated dicarboxylic acid anhydride and a vinyl or vinylidene monomer at a temperature in the range 70 to 145°C. to evolve ammonia or alkylamine.

The reaction may be represented as:—



where X represents the vinyl residue in the copolymer, R is hydrogen or alkyl, and n is an integer greater than 1.

The amide-ammonium or alkyl-substituted amide-alkylammonium salt may be heated in solid form, for example as a dry powder on a tray or in a fluidised bed, or in suspension in an inert liquid, for example toluene or petroleum ether. Heating under reduced pressure facilitates removal of the evolved ammonia or amine.

The amide-ammonium or alkyl-substituted amide-alkylammonium salt may be prepared in known manner by reacting the copolymer of an α,β -unsaturated dicarboxylic acid anhydride and a vinyl or vinylidene monomer with ammonia or an alkylamine.

Convenient amide-ammonium and alkyl-substituted amide-alkylammonium salts include the amide-ammonium and propylamide-propylammonium salts of methyl vinyl ether/maleic anhydride copolymers. The amide-ammonium salts of vinyl acetate/maleic anhydride and ethylene/maleic anhydride copolymers also may be used.

The thickening agents of the invention usually give solutions of higher viscosity than solutions of the copolymer salt from which they are derived. They are useful for

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thickening aqueous media and in adhesives. Those derivatives which give low viscosity aqueous solutions are valuable "plumping" agents for leather tanning, in which applications the fully substituted amide-ammonium salts are not effective and the partially substituted amide-ammonium salts, although useful, are not satisfactory because of their non-uniform constitution and slow rate of solution.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight.

EXAMPLE 1

The amide-ammonium salts of samples of water-soluble methyl vinyl ether/maleic anhydride alternating copolymers of various molecular weights were prepared by suspending 10 parts of copolymer in 100 parts of toluene and reacting with excess ammonia to form the copolymer amide-ammonium salts in suspension.

The amide-acid derivatives were prepared from these amide-ammonium salt suspensions by heating them under reflux (ca. 110°C.) with stirring for six hours, during which time ammonia was evolved. The products were then filtered off and dried free of toluene in air or in a vacuum. Yields of 10-11 parts were obtained.

These products, which were slightly off-white powders, dissolved in cold water (ca. 15°C.) within 20 minutes. Solutions were made up to 5% solids for the lower molecular weight materials and 1% solids for the higher molecular weights and the viscosities of these solutions were measured using a Brookfield LV Viscometer at speed 12 and 25°C. These solutions were found to have a pH of about 4.

The viscosities of these amide-acid solutions and their relationship with the viscosities of the amide-ammonium salt starting materials are summarized in the following table, together with analyses obtained for these particular products. The theoretical composition of fully-substituted amide-acid derivative of methyl vinyl ether/maleic anhydride copolymer, $(C_7H_{11}O_4N)_n$, is C, 48.55%; H, 6.40% and N, 8.09%.

TABLE

	Sample 1	Sample 2	Sample 3	Sample 4
Viscosity of amide-ammonium salt solution (centipoises)	47	512	525	7,000
Viscosity of amide-acid solution (centipoises)	63	43,000	4,200	19,000
%solution	5	5	1	1
Spindle	1	4	4	4
Analyses				
C%	46.6	48.9	45.3	47.6
H%	6.63	6.03	6.86	6.79
N%	8.49	7.14	8.28	9.04

The infra-red spectra of these amide-acid derivatives were all similar and when compared to those of the amide-ammonium salts were in accord with the transformation of the ammonium salt into a free acid group. Thus the amide-ammonium salts showed absorptions for the carbonyl stretching frequencies at 6.1μ for amide and 6.49μ for the carboxylate anion, whereas the amide-acid showed absorptions at 5.9μ for free carboxylic acid and 6.1μ for amide, with no absorption at 6.49μ . The amide-acid spectrum also showed slight absorptions at $5.45, 5.65\mu$, probably due to traces of imide or anhydride produced by further reaction of the amide-acid.

EXAMPLE 2

A sample of the amide-ammonium salt of methyl vinyl ether/maleic anhydride alternating copolymer prepared as described for sample 3 of Example 1 was dried

free of toluene and spread out in a tray and heated in an oven at 110°C. for six hours to give an amide-acid derivative of the copolymer.

The amide-acid derivative obtained had the same infra-red spectrum as the amide-acid derivatives prepared in Example 1 and its analysis was C, 46.11%; H, 6.97%; N, 7.32%.

A 5% aqueous solution of the derivative had pH 4 and a viscosity of 4,000 centipoises at 25°C., measured by a Brookfield LV Viscometer at speed 12, spindle 4.

EXAMPLE 3

The propylamide-propylammonium salt of the methyl vinyl ether/maleic anhydride alternating copolymer which was used to prepare the amide-ammonium salt, sample 1 in Example 1, was prepared by suspending 75 parts of the copolymer in 500 parts hexane and reacting it with 72 parts of n-propylamine at 70°C. for one hour. The solid product was filtered off and dried in a vacuum.

5 parts of the dried solid dissolved in 95 parts cold water to give a solution with pH 8 and a viscosity of 52.5 centipoises at 25°C., measured by a Brookfield LV Viscometer at speed 12, spindle 1.

The propylamide-acid derivative was prepared from this salt by heating a sample of it in an evacuated vessel at a temperature of 110°C. for seven hours. The product was an off-white powder and it dissolved readily in cold water; a 5% solution had pH 4 and a viscosity of 12 centipoises at 25°C., measured by a Brookfield LV Viscometer at speed 12, spindle 1. The analysis of the product was C, 54.75%; H, 8.38%; N, 6.69%. The theoretical composition of a fully-substituted propylamide-acid derivative of methyl vinyl ether/maleic anhydride copolymer, $(C_{11}H_{11}NO_4)_n$ is C, 55.8%; H, 7.96%; N, 6.51%.

The infra-red spectrum of the propylamide-propylammonium salt showed absorptions of carbonyl stretching frequencies at 6.15 μ and 6.45 μ for secondary amide, (absorption for carboxylate anion at 6.43 μ was probably screened by the 6.45 μ secondary amide absorption). The propylamide-acid product showed an additional absorption at 5.95 μ , a change in accord with the production of a free carboxylic acid group.

EXAMPLE 4

The amide-ammonium salt of a vinyl acetate-maleic anhydride alternating copolymer was prepared as a slurry in toluene by the method described in Example 1. A sample of this amide-ammonium salt was filtered and dried in vacuum. It dissolved in cold water to give a solution with pH 7 and a viscosity, for a 5% solution, of 1,500 centipoises at 25°C., measured by a Brookfield LVT Viscometer with spindle 2, speed 3.

The slurry of this amide-ammonium salt was stirred and heated under reflux for seven hours during which time ammonia was evolved. The pink polymer produced was filtered off and dried in vacuum. The product gave an 0.5% solution in cold water with a pH of 4 and a viscosity of 88,000 centipoises at 25°C. measured with Brookfield spindle 4 and at speed 3.

The infra-red spectrum of this product showed changes similar to those described in Example 1 when compared to that of the amide-ammonium salt. The amide-ammonium salt showed carbonyl absorptions at 5.85 μ for the acetate group from the vinyl acetate-derived component of the copolymer, and at 6.1 and 6.45 μ for amide and carboxylic acid anion respectively; the product had no absorption at 6.45 μ , the amide (6.1 μ) absorption remained unchanged and the acetate absorption at 5.85 μ was strengthened by the co-occurrence of the absorption for carboxylic acid carbonyl group.

An analysis of this product gave C, 48.85%; H, 5.77%; N, 6.91%; a fully substituted amide-acid derivative of vinyl acetate-maleic anhydride copolymer requires C, 47.76%; H, 5.51% and N, 6.96%.

EXAMPLE 5

The amide-ammonium salt of an ethylene-maleic anhydride alternating copolymer was prepared as a slurry in toluene as described in Example 1. A 5% solution of a dried sample of this salt had pH 7 and a viscosity at 25°C. of 4,600 centipoises with Brookfield spindle 3, and speed 2.

The slurry was stirred and heated under reflux for seven hours; then filtered and the solid dried in vacuum. The product was the amide-acid derivative of ethylene-maleic anhydride copolymer.

A 1% solution of this copolymer was prepared by dissolving 2 parts of it in 198

parts of cold water. This solution had pH 4 and a viscosity of 36,000 centipoises with Brookfield spindle 3, and speed 3.

The infra-red spectra of the amide-ammonium salt and amide-acid showed the same carbonyl absorptions as were described in Example 1 for methyl vinyl ether/maleic anhydride copolymer.

An analysis of this product gave C, 47.95%; H, 6.79% and N, 9.95%; a fully substituted amide-acid derived from ethylene-maleic anhydride copolymer requires C, 50.34%; H, 6.34% and N, 9.79%.

WHAT WE CLAIM IS:—

1. A process for the preparation of an amide-acid derivative of an alternating copolymer of an alpha-beta unsaturated dicarboxylic acid anhydride and a vinyl or vinylidene monomer comprising heating a substantially anhydrous water-soluble or water-swellaable amide-ammonium or alkyl-substituted amide-alkylammonium salt of the alternating copolymer at a temperature in the range of 70 to 145°C. to evolve ammonia or alkylamine.
2. A process as claimed in Claim 1 wherein the amide-ammonium or alkyl-substituted amide-alkylammonium salt is heated in solid form.
3. A process as claimed in Claim 2 wherein the amide-ammonium or alkyl-substituted amide-alkyl ammonium salt is heated as a dry powder on a tray or in a fluidised bed or in suspension in an inert liquid, e.g. toluene or petroleum ether.
4. A process as claimed in any one of Claims 1 to 3 wherein the amide-ammonium or alkyl-substituted amide-alkylammonium salt is heated under reduced pressure.
5. A process as claimed in any one of Claims 1 to 4 wherein the amide-ammonium or alkyl-substituted amide-alkylammonium salt is obtained by reacting the alternating copolymer of an alpha-beta unsaturated dicarboxylic acid anhydride and a vinyl or vinylidene monomer with ammonia or an alkylamine.
6. A process as claimed in Claim 5 wherein the alkylamine is n-propylamine.
7. A process as claimed in any one of Claims 1 to 6 wherein the copolymer is a copolymer of maleic anhydride with methyl vinyl ether, ethylene or vinyl acetate.
8. A process for the preparation of an amide-acid derivative of an alternating copolymer of an alpha-beta unsaturated dicarboxylic acid anhydride and a vinyl or vinylidene monomer substantially as herein described with reference to the Examples.
9. An amide-acid derivative of an alternating copolymer of an alpha-beta unsaturated dicarboxylic acid anhydride and a vinyl or vinylidene monomer whenever prepared by a process as claimed in any one of Claims 1 to 8.
10. A thickening agent comprising an aqueous solution of an amide-acid derivative as claimed in Claim 9.

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